ON THE INVESTIGATION OF THE

THERMO-LUMINESCENT CURVE

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- COMMUNIST CHINA -

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FOREWORD

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1. When the condition of excitation (e.g., change
in excitation intensity) to phosphorescent material changes,
there is always some delay in the corresponding luminous
intensity change. This is mainly caused by the fact that
in phosphorescent material either electrons or holes can
be captured by the localized energy level, the main char-
acteristic of the captured energy level being its depth.
Among the methods for determining the depth of the captured
energy level, the one which studies the thermo-luminescent
curve seems to be most effective and convenient. In the
above study there are two commonly adopted theorems upon
which the study is based. One theorem assumes that the
recombination process obeys the mono-molecular reaction rule,
while the other assumes that the recombination process obeys
the simple, bi-molecular reaction rule. From the viewpoint
of the energy band model (neng tai mo hsing), they corres-
pond to two limiting cases: the ratio of the probability
of recombination to that of capture approaches or it
approaches zero. Although there has been data published
which enables us to estimate the extreme to which the
actual situation is likely to approach, when determining
the depth of the energy level we can treat it as only one
of the limiting cases. As it is known, the depth of the
energy level obtained from treating it in two limiting
cases differs by a factor of 2. In a typical phosphorescent

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material such as zinc sulfide, as shown in (5), the probability of electron recombination is almost equal to the probability of capture. Therefore, in order to accurately estimate the energy level, it is necessary to take into account the ratio of probability of recombination to that of capture. Therefore, in this paper, we investigate the thermo-luminescent curve as follows.[1]

2. From the viewpoint of energy band model (neng tai mo hsing), it is not difficult to deduce the following characteristics: Assuming the electron captured energy level has only one depth, there is only a very small part of energy level which can be filled by electrons, since the electrons once captured have to return to the conducting band before possible recombination with the hole takes place (through external quenching). At any instant t of the thermo-luminescent process

$$\frac{dn}{dt} = -\sigma_0 n u N,\qquad(1)$$

$$\frac{dn_1}{dt} = \sigma v u N - p_0 e^{-\frac{\epsilon}{kT}} n_1.\qquad(2)$$

Since the life of an electron in the trap is longer than when it is in the energy band, $n \simeq n_1$, from (1) and (2) we get

$$\left(1 + \frac{\sigma v}{\sigma_0 n}\right)\frac{dn}{dt} = p_0 e^{-\frac{\epsilon}{kT}} n.\qquad(3)$$

Let

$$n = \gamma n_0, \quad \bar{n}_0 = \frac{\sigma_0 n_0}{\sigma v},\qquad(4)$$

We have

$$\ln\left(\frac{1 + \gamma \bar{n}_0}{\gamma^2}\frac{dn}{dt}\right) = C - \frac{\epsilon}{k}\cdot\frac{1}{T}.\qquad(5)$$

From this relation we see that if we can estimate the value of $\bar{n}_0$, we can plot a straight line from the experimental data and the slope of that straight line gives the value of ϵ. Or, in other words, it is only justified to use all the data after the value of $\bar{n}_0$ is estimated. When we treat the actual case as one of the two extremes, i.e., considering $\bar{n}_0 \sim 0$ or $\bar{n}_0 \to \infty$, it seems justified to use either the first part or the last of the curve, but not both.

Since at any instant, the luminous intensity $I = -\frac{dn}{dt}$ if we make the line $I = h$ intercept with the thermo-luminescent curve, then $\frac{dn}{dt}$ are equal at two intercepting points.

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(1) This is a completed segment of the 1957 work on the luminescent problem. The remainder has not been continued.

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Making use of (5) we get:

$$\ln\left\{\frac{\gamma(1+\gamma\hbar_o)}{\gamma(1+\gamma\hbar_o)}\right\} = \left(\frac{\epsilon}{T_o} - \frac{1}{T_1}\right)\frac{1}{k}. \tag{6}$$

Taking different values of A to obtain corresponding ϵ, and average the value of ϵ.

Finally, when luminous intensity reaches its peak value, its first derivative should be zero. At this peak value of luminous intensity, letting $\frac{dI}{dt}=\beta$, we obtain another relation

$$\epsilon = \left\{\frac{(2+\gamma\hbar_o)}{\gamma(1+\gamma\hbar_o)}\frac{1}{\hbar_o}\frac{dn}{dt}k^2\right\}_m. \tag{7}$$

Subscript m denotes that all quantities in the bracket should be the values corresponding to peak luminous intensity.

If $\hbar_o$ is known, from (6) and (7) we can find ϵ. The quantity ϵ, determined by the above relations, corresponds to the thermo-ionization potential of the captured center. As to internal quenching, as long as its variation is due to temperature under experimental conditions, it is not large. The value of γ does not change, hence the result is not affected.

To estimate $\hbar_o$, we can use the method suggested by (6), but upon careful analysis of (5), we can also determine both $\hbar_o$ and ϵ simultaneously from the thermo-luminescent curve itself by making use of the characteristics reflected (5). In fact, if we let $\hbar_o$ change from 0 to ∞, the plot of $\ln\left(\frac{2+\gamma\hbar_o}{\hbar_o}\frac{dn}{dt}\right)$ against $\frac{1}{T}$ will become straightened gradually from inclining to a certain direction and then inclines to another direction. When the straight line appears, it means that the value of $\hbar_o$ in compliance with the actual condition is found (within the range of temperature change in the experiment the change of $\frac{dn}{dt}$ with temperature is neglected for the time being).

3. In order that the thermo-luminescent curve is not affected by shallow energy level, we first excite a sample (ZnS-Cu, Co, in which Cu has 10^{-6}, Co has 10^{-5} gm/gm it is made from heating 5% $CaCl_2$ at a temperature of $1100^\circ c$ for 30 min.) at $65^\circ c$, then let the luminescence fade 15 min. and cool it to the temperature of liquid air. Heat it in such a way that the temperature rises uniformly, using ЭЗУ-19 and ammeter to detect the variation of the

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(1) The author of (7) mentioned, in general, by the change of $\ln\frac{1}{T}$ and $\ln\frac{1}{\hbar}$ with T^{-1} and its deviation from linear relationship, $\hbar_o$ can be determined-- remarked when editing.

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luminous intensity to obtain thermo-luminescent curve as
shown in fig. 1.

Fig. 1 t(min)

(a) Thermo-luminescent curve, first excite Zns-Cu,
    Co at 65°c with ultraviolet light of 366mμ,
    then cool a sample with liquid air, wait until
    the temperature reaches the lowest steady
    state, then start to measure.
(b) Temperature change with change of time when
    measuring thermo-luminescent curve.

Straight lines show that the temperature rises with time.
Fig. 2 shows that when $\bar{n}$ is about 3, a straight line can
be obtained, from the slope of the straight line is found
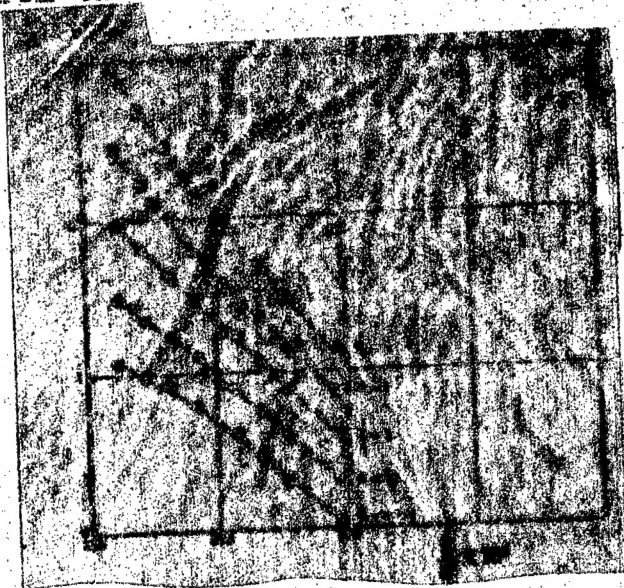to be $\varepsilon = 0.83$ev.

Fig. 2.   Relation between ░░░░░░░. and $\frac{1}{T}$

At this stage we need not use (6) because it only represents a part of (5), but we still can use (7). Values of σ, σ_o pass the plot of α versus t, n_o measure the slope; or from the ratio of luminous intensity to find the slope. $\beta = 9.2/\text{min.}, \epsilon = 0.86\text{ev.}$

The meaning of the symbols used in this paper:
- σ_o, σ — effective electron recombination and capture section respectively
- N — density of electron in conducting band
- u — average velocity of moving electrons
- ν — density of electron captured energy level
- n_i — density of electron captured energy level which is fully filled by electrons

 — density of ionization center at $t \neq 0$

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